SPECIFICATION

RELEASE AGENT FOR METALLIC MOLD

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a metallic molds used for release agent for metallic mold for forming of plastic molded product. Products

2. Description of the Related Art

Plastics have excellent properties productivity easy processability, high ctivity, light, weight and relative they are used for s o procuring parts and structural materials metibe, autobicycle, scooter, television radio, audio equipment, washing machine personal computer, portable cooker, telephone, game machinery, building mater Moderals office supplies, stationery, toys, sports equipment, agricul goods, tural tools and marine tools.

They are usually prepared by plastic processing methods such as injection molding, blow molding, compression molding, transfer molding, rotating molding, slush molding, inflation tubular film process, and extrusion molding. Processes,

As plastics processing are conducted temperatures above 200°C, additives, monomers, decomposed materials in the plastics are changed to carbonized make-waterials such as tar, pitch and other coloured sticky substances, which are apt to adhere to the surface of the screw, bear-

Svolado

hassel, die and metallic mold of the plas-plastic tie processing machine to cause transfer of the carbonized materials to the mol molded ded product. Placed Makes

Above mentioned transfer make the sur- surfaces makes face of molded product dirty and make the dimensions of the molded product uninaccually accurate; not the perform expected moving of structual function, therefore clean-claumy ing the screw, barrel, die and metallic mold of the plastic processing machine machines has been required.

Change Specific

In case of production change from specific colored molded article to noncolved cutred or ether colored molded article; oured or ether soloured molded article; cleaning the screw, barrel and die has confamination been also required to avoid cross contamination residual specifical colored residual compositions

However there are some problems on the conventional cleaning method of the screw, barrel, die and metallic mold.

There are some problems occurring at assiculed with releasing the plastic molded product products molds.

from metallic molds used

The metallic mold for forming the planstic molded products have sometimes the planstic molded product has the complicated shape with fine hollow and convex parts products

Therefore, the plastic molded product

such as mechanical parts for electronic

devices and automobile has the complicated

shapes consequently it is difficult to

release the plastic mold products from

metallic mold, because both surface has

the complicated contrasting shape, which

causes plastic mold product ingrowing to

Cause A

and become anchored thereto to cristing metallic mold as if anchor bites rock of bottom of the sea.

difficulty To avoid above mentioned S H T T a C O, both releasing face between the metallic mold and the plastic molded product. the method for giving lublicant has been conventionally use

the release agent for metallic mold. nolds

lublicant is usually applied by it on the metallic mold surface sweet,

However, when the metallic mold coated by the conventional release agent was 15 by the conventional release

by the conventional release

used for a long time, hard and uneven he release

used for a long time, hard and uneven he release

to the following terogeneous layer was formed by the accomulation Lowing reasons.

One reason is accumlation of the resin and its additives such as antioxdant nucleating agent, an auti-ultraviolet metal deactivater, agent, antistatic agent, tiul traviole t crosslinking agent, valcanization agent5 and lublicants

The other reason is accumulation of the decomposition materials of resin and its additives.

The uneven shape on the surface of me metallic tallic mold, apt to be transfered on the surface of the plastic molded product together with accomplated contaminants on the surface of the metallic mold are adhered to the surface of the plastic molded transtermen product.

Above mentioned tranafering of shape makes the dimensions of the plastic molded product unaccurate, not to perform maccivate

required novement of structural function, a confaunt makes the surface of the plastic molded product dirty.

The hard and uneven heterogenous layer on the surface of the metallic mold fur sufface face makes releasing property, wrong.

To remove the contaminants and heterogenous layer on the surface of the metallic mold, it is general way to wash the
soiled metallic mold after using predetermined
ermined—time.

facily use

washing is curried out after troublesome task of taking the soiled metallic mold out from plastic processing machine, and taking the plastic mold to pieces, which requires times and labor to cause heavy loss are efficiency and cost.

Especially at complicated or large sized metallic mold, removing, demanting and and washing work are tremendous to eause obstacles to improving the productivity and cost down.

To decrease the number of times of the metallic mold washing, a release agent have

As the release agent, there has been known many types of that such as dimeth-dimethyl yl polysiloxane of the non-closs linking type, paraffin wax, higher fatty acid derivat-derivatives iver metal saap, talc, mica, and polytetaflooloothylene raftuoroethylene of crosslinking type, and the like.

However, conventional release agent have have the following draw-

In case employing a non-closslinking type of release agent, the release agent stay stays in specific place of the metallic mold so as to affect back influence for the plastic molded product.

In tase temploying crosslinking type of the release agent, it exhibits to excellent release agent, it exhibits to excellent release agent apt to adhere to the surface of a plastic molded product to prevent the uniform painting or adhering treatment, resulting to decrease postprocessability.

a sufficient releasure In case of requiring, a_{short} shot cycle achieve sing effect to time, the amount of release agent must be increased, resulting to a-e-e- ocur, the umulation and degradation of the release This Co on the metallic molda the smooth and gross properties and degradation of the chanical fluence t-0 such as tensile, elongate and strength.

Further, it has become the problem that the release agent itself has decomposed by the high temperatur heat transfer from the metallic mold.

For instance, dimethyl polysiloxane oil wholes the sentative release agent has temperative been gradually decomposed over the temperative exature of 150°C and has been rapidly decomposes composed over the temperature of 200°C to make it is materials, which has become the problem to degrade the releasing property.

For improving the heat-resistant per -

perty of the sand dimethyl polysiloxane, the use of
the re has been proposed the aminogroup
mercaptogroup modified dimethyl polysiloxane dysloxane has been proposed.
However, there has been detected that
problem that said modified dimethyl
guerales
polysiloxane has generated bad smell

or mercaptan and has

Also, dimethyl polysiloxane has been a celest agent using dimethyl polysiloxane must has been prepared by dispersing it in the water to form the micelles using a surface active agent, because dimethyl polysiloxane itself is not compatible

ammonia gas

The release agent using polytetrafluor roethylene has the drawback that it must be baked onto the surface of metallic mold, therefore many troublesome repeater repeated ing work of baking must be conducted notwithstanding its excellent releasing effect and secondary processing property properties.

It is desirable that the release agent molds be for metallic mold is prepared as the an emulsion type from viewpoint of cost, applicability.

ability.

agus all

method that surface active agent, water and non-water-soluble dimethyl polysilo-pared by the surface active agent, water and non-water-soluble dimethyl polysilo-pared fourthing to a surface and solubles agent agent agent fourthing micelles are all to be diapersed into water.

However, above mentioned surface active

agent reacts with the ingredients bleed agent reacts with the ingredients bleed of from plastic molded product to form the strong membrane (coated layer) on the surface of the metallic mold.

The membrane (coated layer) has hard and has an and whether of the regeneous shape there fore the shape is trasfered on the surface fore the shape is trasfered on the surface ace of the plastic molded product to cause the problem of product to factors the problem of product. Products

On the other hand, when above mentioned release agent of crosslinked type by that seguing baking is used, the baked membrance (coated layer) the exhibiting the releasing effect has been gradually scraped, by the

metallic mold at each injection shot. celeuse As the above mentioned baked type release agent is gradually scraped at each shot of plastic resin composition into metallic mold, the release agent is removed from the surface of metallic mold by repeating shots from it to 20 repertations. Then from 10 to 20 shots were over,

resin composition contacting t# the

fresh Then from 10 to 20 shots were other, the release agent must be applied onto the surface of metallic mold, which is uvery troublesome works.

Further habove mentioned baked type release agent has the other problem owing
to containing the reactive functional
group such as amino, mercapto, isocyanate
or vinyl group which is used for conductory
time crosslinking and baking reaction on
the surface of metallic mold.

Owing to the reactive functional group, the surface energy of the releasing

very large to mincrease the frictional force between the surface of the plastic molded product and the surface of release agent layer, which causes consumption of the release agent layer by scraping restrict the life of mrelease agent layer first the term of from 10 to 20 shots of injection mold. Material

Short life of the release agent requirement from the lime of the release agent by the accumulation baking treatment, which lead to accumulate lation of the unnecessary baked crossli-crosslinked need release agent on the surface of the metallic mold, which affects bad influenters such as shape and contaminant transfer fering to the plastic molded product.

As mentioned above, conventional type release agent has the drawback such as poor release effect, short durability term, difficult secondary processability and difficult treatment (baking) work on to the metallic mold.

SUMMARY OF THE INVENTION

As a result of diligent investigation dura the course of invention, under such situation, the present invention provides a release agent for metallic mode for formy ming a plastic molded product character containing a borate ester of a polyoxyalkylene.

DETAILED DESCRIPTION OF THE INVENTION

A borate ester of polyoxyalkylene used for the present invention is a chemical compound expressed by the following general formula (1).

$$R^{1} = \left(0\text{CH}_{2}\text{CH}_{2}\right)_{a} \left(0\text{CH}_{2}\text{CHCH}_{3}\right)_{b} = 0$$

$$R^{2} = \left(0\text{CH}_{2}\text{CH}_{2}\right)_{c} \left(0\text{CH}_{2}\text{CHCH}_{3}\right)_{d} = 0$$

$$R^{3} = \left(0\text{CH}_{2}\text{CH}_{2}\right)_{e} \left(0\text{CH}_{2}\text{CHCH}_{3}\right)_{f} = 0$$
(1)

wherein R¹, R² and R³ are independently selected from group consisting of hydromy hydrography a, b, c, d, e and f are positive integers independently selected from 0 to 30 whose sum is from 6 to 80.

Example of the hydrocarbon group are alkyl groups such as methyl, ethyl, pro-propyl pyl, isopropyl, buthyl, penthyl, hexyl, octable nonyl, decyl, dodecyl, hexadecyl, octadecyl and docosyl groups and phenyl, tolyl and cyclohexyl groups and phenyl,

Illustrative of the borate cater of polyoxyalkylene are the chemical compound expressed by the following chemical formula from (2) to (27).

$$\begin{array}{c} \text{CH}_{\frac{1}{3}}\left(\text{OCH}_{2}\text{CH}_{\frac{1}{2}}\right)_{\frac{1}{3}}\left(\text{OCH}_{2}\text{CHCH}_{\frac{1}{3}}\right)_{\frac{1}{3}} = 0 \\ \text{CH}_{\frac{1}{3}}\left(\text{OCH}_{2}\text{CH}_{\frac{1}{2}}\right)_{\frac{1}{3}}\left(\text{OCH}_{2}\text{CHCH}_{\frac{1}{3}}\right)_{\frac{1}{3}} = 0 \end{array} \tag{2}$$

$$\begin{array}{c} \text{CH}_{3} \frac{1}{4} \text{OCH}_{2} \text{CH}_{2} \frac{1}{2} \frac{1}{5} \frac{1}{4} \text{OCH}_{2} \text{CHCH}_{3} \frac{1}{2} = 0 \\ \text{CH}_{3} \frac{1}{4} \text{OCH}_{2} \text{CH}_{2} \frac{1}{2} \frac{1}{5} \frac{1}{4} \text{OCH}_{2} \text{CHCH}_{3} \frac{1}{2} = 0 \\ \text{CH}_{3} \frac{1}{4} \frac{1}{4} \text{OCH}_{2} \text{CH}_{2} \frac{1}{2} \frac{1}{5} \frac{1}{4} \text{OCH}_{2} \text{CHCH}_{3} \frac{1}{2} = 0 \end{array}$$

$$C_{2}H_{5} \left(OCH_{2}CH_{2} \right) \frac{1}{8} \left(OCH_{2}CHCH_{3} \right) \frac{1}{2} O$$

$$C_{2}H_{5} \left(OCH_{2}CH_{2} \right) \frac{1}{5} \left(OCH_{2}CHCH_{3} \right) \frac{1}{3} O$$

$$CH_{3} \left(OCH_{2}CH_{2} \right) \frac{1}{2} \left(OCH_{2}CHCH_{3} \right) \frac{1}{7} O$$

$$(4)$$

$$\begin{array}{c} \text{CH}_{\frac{1}{3}} \left(\text{OCH}_{2} \text{CH}_{\frac{1}{2}} \right)_{\frac{1}{3}} \left(\text{OCH}_{2} \text{CHCH}_{\frac{1}{3}} \right)_{\frac{1}{3}} \text{O} \\ \text{H} \left(\text{OCH}_{2} \text{CH}_{\frac{1}{2}} \right)_{\frac{1}{3}} \left(\text{OCH}_{2} \text{CHCH}_{\frac{1}{3}} \right)_{\frac{1}{3}} \text{O} \\ \text{CH}_{\frac{1}{3}} \left(\text{OCH}_{\frac{1}{2}} \text{CH}_{\frac{1}{2}} \right)_{\frac{1}{3}} \left(\text{OCH}_{\frac{1}{2}} \text{CHCH}_{\frac{1}{3}} \right)_{\frac{1}{3}} \text{O} \end{array}$$

$$H = \frac{\left(0\text{CH}_{2}\text{CH}_{2}\right)_{7}\left(0\text{CH}_{2}\text{CHCH}_{3}\right)_{2}}{0\text{CH}_{2}\text{CH}_{2}\right)_{7}\left(0\text{CH}_{2}\text{CHCH}_{3}\right)_{2}} = 0$$

$$CH_{3} = \frac{\left(0\text{CH}_{2}\text{CH}_{2}\right)_{7}\left(0\text{CH}_{2}\text{CHCH}_{3}\right)_{2}}{0\text{CH}_{2}\text{CHCH}_{3}\right)_{2}} = 0$$
(6)

$$H = \frac{\left(\text{OCH}_{2}\text{CH}_{2}\right)_{5}\left(\text{OCH}_{2}\text{CHCH}_{3}\right)_{1}}{\left(\text{OCH}_{2}\text{CH}_{2}\right)_{5}\left(\text{OCH}_{2}\text{CHCH}_{3}\right)_{1}} = 0}$$

$$H = \frac{\left(\text{OCH}_{2}\text{CH}_{2}\right)_{5}\left(\text{OCH}_{2}\text{CHCH}_{3}\right)_{1}}{\left(\text{OCH}_{2}\text{CHCH}_{3}\right)_{1}} = 0}$$

$$(7)$$

$$\begin{array}{c}
CH_{3} - \left(OCH_{2}CH_{2}\right)_{5} - O \\
CH_{3} - \left(OCH_{2}CH_{2}\right)_{5} - O
\end{array}$$

$$CH_{3} - \left(OCH_{2}CH_{2}\right)_{5} - O$$

$$CH_{4} - \left$$

$$CH_{3} - \left(OCH_{2}CH_{2}\right)_{15} - O$$

$$C_{2}H_{5} - \left(OCH_{2}CH_{2}\right)_{13} - O$$

$$CH_{3} - \left(OCH_{2}CH_{2}\right)_{15} - O$$

$$CH_{3} - \left(OCH_{2}CH_{2}\right)_{15} - O$$

$$(9)$$

$$CH_{3} + (OCH_{2}CH_{2})_{5} = 0$$
 $CH_{3} + (OCH_{2}CH_{2})_{6} = 0$
 $CH_{3} + (OCH_{2}CH_{2})_{7} = 0$
 $CH_{3} + (OCH_{2}CH_{2})_{7} = 0$
 $CH_{3} + (OCH_{2}CH_{2})_{7} = 0$

$$H - \frac{(OCH_{2}CH_{2})_{3}}{(OCH_{2}CH_{2})_{3}} = 0$$

$$CH_{3} - \frac{(OCH_{2}CH_{2})_{3}}{(OCH_{2}CH_{2})_{3}} = 0$$

$$CH_{3} - \frac{(OCH_{2}CH_{2})_{3}}{(OCH_{2}CH_{2})_{3}} = 0$$

$$H - \frac{(OCH_{2}CH_{2})_{20}}{(OCH_{2}CH_{2})_{20}}O B$$

$$H - \frac{(OCH_{2}CH_{2})_{20}}{(OCH_{2}CH_{2})_{20}}O$$

$$H - \frac{\left(OCH_{2}CH_{2}\right)_{7} - 0}{C_{4}H_{9} + \left(OCH_{2}CH_{2}\right)_{7} - 0} B \qquad (13)$$

$$C_{4}H_{9} + \frac{\left(OCH_{2}CH_{2}\right)_{7} - 0}{C_{4}H_{9} + \left(OCH_{2}CH_{2}\right)_{7} - 0}$$

$$H = \frac{\left(0CH_{2}CH_{2}\right)_{25} - 0}{H = \left(0CH_{2}CH_{2}\right)_{25} - 0} B \qquad (14)$$

$$H = \frac{\left(0CH_{2}CH_{2}\right)_{25} - 0}{\left(0CH_{2}CH_{2}\right)_{25} - 0}$$

$$H - \frac{(OCH_{2}CH_{2})_{6}}{(OCH_{2}CH_{2})_{1}} = 0$$

$$C_{8}H_{17} + \frac{(OCH_{2}CH_{2})_{1}}{(OCH_{2}CH_{2})_{6}} = 0$$

$$C_{4}H_{9} + \frac{(OCH_{2}CH_{2})_{6}}{(OCH_{2}CH_{2})_{6}} = 0$$
(15)

$$CH_{3} \frac{\left(OCH_{2}CH_{2}\right)_{6}\left(OCH_{2}CHCH_{3}\right)_{2}}{CH_{3}} \frac{\left(OCH_{2}CH_{2}\right)_{6}}{\left(OCH_{2}CH_{2}\right)_{6}}O$$

$$CH_{3} \frac{\left(OCH_{2}CH_{2}\right)_{8}\left(OCH_{2}CHCH_{3}\right)_{3}}{OCH_{2}CHCH_{3}}O$$

$$CH_{3} \frac{\left(OCH_{2}CH_{2}\right)_{8}\left(OCH_{2}CHCH_{3}\right)_{3}}{OCH_{2}CHCH_{3}}O$$

$$C_{2}H_{5} \frac{\left(OCH_{2}CHCH_{3}\right)_{8}}{\left(OCH_{2}CH_{2}\right)_{20}}O \qquad B \qquad (17)$$

$$C_{2}H_{5} \frac{\left(OCH_{2}CH_{2}\right)_{8}}{\left(OCH_{2}CHCH_{3}\right)_{2}}O$$

$$C_{4}H_{9} \left(-0CH_{2}CH_{2}\right)_{5} - 0$$

$$C_{3}H_{7} \left(-0CH_{2}CH_{2}\right)_{8} - 0$$

$$CH_{3} \left(-0CH_{2}CH_{2}\right)_{18} \left(-0CH_{2}CH_{2}\right)_{5} - 0$$
(18)

$$CH_{\frac{1}{3}} \frac{\left(OCH_{2}CH_{\frac{1}{2}}\right)_{9} - \left(OCH_{2}CHCH_{\frac{1}{3}}\right)_{7} - 0}{H - \left(OCH_{2}CH_{\frac{1}{2}}\right)_{15} - 0} B \qquad (19)$$

$$CH_{\frac{1}{3}} \frac{\left(OCH_{2}CH_{\frac{1}{2}}\right)_{13} \left(OCH_{2}CHCH_{\frac{1}{3}}\right)_{11} - 0}{H - \left(OCH_{\frac{1}{2}}CH_{\frac{1}{2}}\right)_{13} + OCH_{\frac{1}{2}}CHCH_{\frac{1}{3}}\right)_{11} - 0}$$

$$H = \frac{\left(\text{OCH}_2\text{CHCH}_3\right) - 0}{H - \left(\text{OCH}_2\text{CH}_2\right) - 0} B \qquad (20)$$

$$C_2H_5 = \left(\text{OCH}_2\text{CH}_2\right) - \frac{1}{3} \left(\text{OCH}_2\text{CHCH}_3\right) - \frac{1}{3} \left(\text{OCH}_2\text{$$

$$H = \frac{\left(0CH_{2}CH_{2}\right)_{21}}{\left(0CH_{2}CH_{2}\right)_{7}} = 0$$

$$H = \frac{\left(0CH_{2}CH_{2}\right)_{15}}{\left(0CH_{2}CH_{2}\right)_{15}} = 0$$
(21)

$$CH_{3} \frac{\left(OCH_{2}CH_{2}\right)_{6} \left(OCH_{2}CHCH_{3}\right)_{2}}{C_{2}H_{5}O} B \qquad (22)$$

$$CH_{3} \frac{\left(OCH_{2}CH_{2}\right)_{6}}{OCH_{2}CH_{2}\right)_{6}} O$$

$$CH_{3} - \left(OCH_{2}CH_{2}\right)_{25} - O$$
 $C_{16}H_{33}O - B$ (23)
 $CH_{3} - \left(OCH_{2}CH_{2}\right)_{25} - O$

$$C_{2}H_{5} \frac{\left(OCH_{2}CH_{2}\right)_{8} \left(OCH_{2}CHCH_{3}\right)_{8}}{HO}B \qquad (24)$$

$$C_{2}H_{5} \frac{\left(OCH_{2}CH_{2}\right)_{8} \left(OCH_{2}CHCH_{3}\right)_{8}}{OCH_{2}CHCH_{3}\right)_{8}}$$

$$H = \frac{\left(\text{OCH}_2 \text{CH}_2 \right)_{20} \left(\text{OCH}_2 \text{CHCH}_3 \right)_5 - 0}{C_2 H_5 0}$$

$$C_3 = \frac{\left(\text{OCH}_2 \text{CH}_2 \right)_{20} - 0}{C_2 H_5 0}$$

$$C_4 = \frac{\left(\text{OCH}_2 \text{CH}_2 \right)_{20} - 0}{C_2 H_5 0}$$

$$C_5 = \frac{\left(\text{OCH}_2 \text{CH}_2 \right)_{20} - 0}{C_2 H_5 0}$$

$$H - \frac{\left(-0CH_{2}CH_{2} - \frac{1}{30} - 0\right)}{C_{16}H_{33}0} B \qquad (26)$$

$$H - \frac{\left(-0CH_{2}CH_{2} - \frac{1}{30} - 0\right)}{C_{16}H_{33}0} C$$

Production method for borate esters of polyoxyalkylene used for the present invention are not limited to specific method but following method is prefered able.

The borate esters of polyoxyalkylene are produced by esterification dehydraction of the sterification of the steri

It is prefavable that reaction is earried out by using 1 mol of boric acid or
borate esters of lower alcohols with from
3 to 3.5 moles of polyoxyalkylene expression
seed by the chemical formula (28).

If the mole ratio is less than 3 it is not prefevable because undesirable byproducts of borate esters having two or three boron atoms are generated.

The other byproducts or unreacted polyoperally lend oxalkylene may be remained in the borate esters unless they do not hinder the purging effect of the resin composition of the present invention.

 R^1 (OCH₂CH₂) a (OCH₂CHCH₃) bOR² (28)

wherein R¹ and R² are independently selected from agroup consisting of hydrogen and hydrocarbon group, a and b are hinderly pendently from 0 to 30.

Example of the hydrocarbon group are alkyl groups such as methyl, ethyl, propyl, isopropyl, buthyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, hexadecyl, oeta-octadecyl decyl and docosyl groups and phenyl, to folyl lyt and cyclohexyl groups.

Example of the polyoxyalkylene expressed seed by the chemical formula (28) are as follows.

monomethyl ether, glycol diethylene monoethyl ether, glycol diethylene monoisopropylether, glycol diethylene mono but ether. glycol diethylene monoctul ether. glycol diethylene monodecyl ether, glycol diethylene monohexadecyl ether, glycol diethylene monooctadecyl ether, glycol diethylene monomethyl ether, glycol triethylene monoethyl ether, glycol triethylene monoisopropylether, triethylene glycol ether, glycol triethylene mono sidel ether, glycol triethylene mondety ether, glycol triethylene monodecyl ether, glycol triethylene glycol monohexadecyl ether, triethylene monooctadecyl ether, glycol triethylene

glycol monomethyl ether, tetraethylene monoethyl ether, glýcol tetraethylene monois, o, propyl ether, glycol tetraethylene moro bul monobuthy 1 ether, glycol tetraethylene t by l ether, glycol tetraethylene

tetraethylene glycol monodecyl ether, tetraethylene glycol monohexadecyl ether, tetraethylene glycol monooctadecyl ether,

monomethyl ether, glycol polyethylene monoethyl ether, glycol polyethylene mono, i so, propyl ether, glycol polyethylene monobutal monobutal ether. glycol polyethylene monooctul monooctul ether, polyethylene glycol monodecyl ether, polyethylene glycol monohexadecyl ether, glycol polyethylene monooctadecyl ether, polyethylene glycol

glycol monomethyl ether, dipropylene monoethyl ether, glycol dipropylene monoisopropyl

Monopolyt

monobuthyl eth ether, dipropylene glycol -r ether. dipropylene glycol monooctal ether, glycol dipropylene monodecyl ether, glycol dipropylene monohexadecyl glycol dipropylene monooctadecyl ether, glycol dipropylene

ether, glycol monomethy l tripropylene monoethyl ether, glycol tripropylene ether, monoi, sopropy l tripropylene glvcol monobolyh manobut ether. tripropylene glycol monooctyl monooctyl ether. glycol tripropylene monodecyl ether, tripropylene glycol monohexadecyl ether, glycol tripropylene monooctadecyl ether, tripropylene glycol

monomethyl ether, glycol tetrapropylene monoethyl ether, tetrapropylene glycol monois, opropylether, glycol tetrapropylene mone buyl monoccyl ether, glycol tetrapropylene monoocthyl ether. tetrapropylene glycol

tetrapropylene glycol monodecyl ether, tetrapropylene glycol monohexadecylether, tetrapropylene glycol monooctadecylether,

polypropylene glycol monomethyl ether, polypropylene glycol monoethyl ether, polypropylene glycol monoisopropyl ether, polypropylene glycol monobuthyl ether, polypropylene glycol monoocthy-lether, polypropylene glycol monodecyl ether, glycol monohexadecyl ether, polypropylene polypropylene glycol monooctadecyl ether.

diethyleneglycol tripropyleneglycol monomethyl ether, tetraethyleneglycol dipropyleneglycol monomethyl methere tetraethyleneglycol tripropyleneglycol monomethyl ether, tetraethyleneglycol tetrapropyleneglycol monomethyl ether, pentaethyleneglycol dipropyleneglycol monomethyl ether. pentaethyleneglycol tripropyleneglycol monomethyl ether, diethyleneglycol tetrapropyleneglycol monomethyl ether,

hexaethyleneglycol dipropyleneglycol monomethyl ether, hexaethyleneglycol dipropyleneglycol monomethyl mether, eller hexaethyleneglycol tripropyleneglycol monomethyl ether, hexaethyleneglycol tetrapropyleneglycol monomethyl ether,

hexaethyleneglycol pentapropyleneglycol monomethyl ether, hexaethyleneglycol hexapropyleneglycol monomethyl ether,

heptaethyleneglycol dipropyleneglycol
monomethyl ether,
heptaethyleneglycol dipropyleneglycol
monomethyl methes eller,
heptaethyleneglycol tripropyleneglycol
monomethyl ether,
heptaethyleneglycol tetrapropyleneglycol
monomethyl ether,
heptaethyleneglycol pentapropyleneglycol
monomethyl ether,
heptaaethyleneglycol hexapropyleneglycol
monomethyl ether,
heptaaethyleneglycol hexapropyleneglycol
monomethyl ether,
heptaaethyleneglycol heptapropyleneglycol

octaethyleneglycol dipropyleneglycol monomethyl ether, octaethyleneglycol tripropyleneglycol monomethyl methers eller. tetrapropyleneglycol octaethyleneglycol monomethyl ether, pentapropyleneglycol octaethyleneglycol monomethyl ether, octaethyleneglycol hexapropyleneglycol monomethyl ether, octaethyleneglycol heptapropyleneglycol monomethyl ether, polyethyleneglycol polypropyleneglycol monomethyl ether,

triethylene glycol,

tetraethylene glycol,

pentaethylene glycol,

hexaethylene glycol,

heptaethylene glycol,

octaethylene glycol,

tridecaethylene glycol,

hexadecaethylene glycol,

eicosaethylene glycol,

pentacosaethylene glycol,

triacosaethylene glycol,

tripropylene glycol,

tetrapropylene glycol,

pentapropylene glycol,

hexapropylene glycol,

octapropylene glycol,

decapropylene glycol,

tridecapropylene glycol,

eicosapropylene glycol,

pentacosapropylene glycol,

triacosapropylene glycol,

triethylene glycol tripropylene glycol, tetraethylene glycol dipropylene glycol, tetraethylene glycol tripropylene glycol, tetraethylene glycol tetrapropylene glycol, pentaethylene glycol dipropylene glycol, pentaethylene glycol tripropylene glycol, hexaethylene glycol dipropylene glycol, hexaethylene glycol tripropylene glycol, hexaethylene glycol pentapropylene glycol,

hexaethylene glycol hexapropylene glycol, heptaethylene glycol dipropylene glycol, triacosaethylene glycol dipropylene glycol, glycol,

heptaethylene glycol tripropylene glycol, heptaethylene glycol tetrapropylene glycol, heptaethylene glycol pentapropylene

heptaethylene glycol pentapropylene glycol,

heptaethylene glycol hexapropylene glycol,

heptaethylene glycol heptapropylene glycol,

octaethylene glycol dipropylene glycol, octaethylene glycol tripropylene glycol, octaethylene glycol tetrapropylene glycol,

octaethylene glycol pentapropylene glycol,

octaethylene glycol hexapropylene glycol, octaethylene glycol pentapropylene glycol,

octaethylene glycol octapropylene glycol, polyethylene glycol polypropylene glycol,

tripropylene glycol triethylene glycol monomethyl ether,

tetrapropylene glycol diethylene glycol monomethyl ether,

tetrapropylene glycol triethylene glycol monomethyl ether,

tetrapropylene glycol tetraethylene glycol monomethyl ether,

pentapropylene glycol diethylene glycol

monomethyl ether,

pentapropylene glycol triethylene glycol

monomethyl ether,

pentapropylene glycol tetraethylene

glycol monomethyl ether,

hexapropylene glycol diethylene glycol monomethyl ether,
hexapropylene glycol triethylene glycol monomethyl ether,
hexapropylene glycol tetraethylene glycol monomethyl ether,
hexapropylene glycol pentaethylene glycol monomethyl ether,
hexapropylene glycol pentaethylene glycol monomethyl ether,

heptapropylene glycol diethylene glycol monomethyl ether,
heptapropylene glycol triethylene glycol monomethyl ether,
heptapropylene glycol tetraethylene glycol monomethyl ether,
heptapropylene glycol pentaethylene glycol monomethyl ether,
heptapropylene glycol pentaethylene glycol monomethyl ether,
heptapropylene glycol hexaethylene glycol monomethyl ether,
heptapropylene glycol heptaethylene glycol monomethyl ether,

octapropylene glycol diethylene glycol monomethyl ether, octapropylene glycol triethylene glycol monomethyl ether, octapropylene glycol tetraethylene glycol monomethyl ether,

octapropylene glycol pentaethylene glycol monomethyl ether,

octapropylene glycol hexaethylene glycol monomethyl ether,

octapropylene glycol heptaethylene glycol monomethyl ether

octapropylene glycol octaethylene glycol monomethyl ether

polypropylene glycol polyethylene glycol monomethyl ether

tripropylene glycol triethylene glycol monomethyl ether,

tetrapropylene glycol triethylene glycol monomethyl ether,

tripropylene glycol triethylene glycol monomethyl ether,

octapropylene glycol diethylene glycol monomethyl ether,

octaethylene glycol dipropylene glycol monomethyl ether,

octaethylene glycol tripropylene glycol monomethyl ether,

octaethylene glycol tetrapropylene glycol monomethyl ether,

octaethylene glycol pentapropylene glycol monomethyl ether,

Soctaethylene glycol hexapropylene glycol

octaethylene glycol heptapropylene glycol monomethyl ether,

octaethylene glycol octapropylene glycol monomethyl ether,

polyethylene glycol polypropylene glycol monomethyl ether.

Incorporata

A solvent or diluent may be in-corporated into the raw materials such as boric acid, borate ester of lower alcohol and polyoxyalkylene, or into horate esters of polyoxyalkylene.

If the solvent or diluent are employed, they must not disturb the esteryfication—dehydration or ester—exchange reaction points shows preferable believe the boiling point are preferable believe the boiling point of the byproductocts or polyoxyalkylenes.

Example of the solvents or diluents are

Example of the solvents or diluents are ethers such as diethyl ether, dioxane, tetrahydrofran; aliphatic hydrocarbons such as hexane, acetic anhydride, heptane, octane, nonane, decane, undecane; aroma acomatic tie hydrocarbons such as benzene, telu-foluent ene, xylene; cycloalkane such as cyclo-cyclohyane hexane, cyclohexene; non-proton polar compounds such as dimethy formamide, di-cimethyl methyl sulfoxide, hexamethyl polyamide phosphate, acetonitrile, N-methyl pyrra-py (collect) lidone; and their chlorine substituted compound such as chloroform and carbon tetrachloride.

tetrachloride.

Catalysts for the esteryfication—
dehydration or ester—exchange reaction
may be used.

If the catalysts are necessary for condensation promoting the reaction, following condensation catalysts are recommended.

Examples Catalysts

Example of the oatalysts are metallic acids such as ferrous one octanuale tanoate, ferrous naphthenate, cobaltous naphthenate, manganese octanoate, stann stannum um octanoate, stannum naphthenate, lead

octanoate, lead naphthenate, organotin tin dioctanoate, dibuty l tin dioleate oxidized dibu é such as tetrabuthyl ti-fituncte tanate, tetrabutyl zirconate; titanium di-isopropoxy bis-acetyl acetonate titanium, 1, 3-propanedioxy 3-propanedory bis-ethylacetonate titanium, bis-ethylacetoacenate titanium; nate; amines such as hexyl amine, dode-dodecylamine eylamine phosphate, dimethyl hydroxy hydroxy diethyl hydroxyamine; tetra ammo-quunonion such las benzyl hydroxyamine; inorganic acid as hydr phosphoricanhydrde nitric acid, sul acid, acid; organic a eid such as acetic ride, pure acetic acid (over 99.8%), pro citric acid. benzoic acid. acetic acid. oxalic p-toluenesulfonic acid; chlorosilanechorosclanes such as methyl trichlorosilane, dimethyl dichlorosilane; inorganic ba aqueous ammonia; organic base ethylene diamine, triethanol amine; and amino alkylamine.

tion dehydration or ester exchange reaction tion is carried out under the condition of at reduced or atmospheric pressure, and ata temperature from 50 to 250°C temperature, favourably and puferally from 100 to 180°C.

During the reaction, removal of bypro-

ducts such as lower alcohol or water can proceed the reaction easily because re- removal moval of byproducts proceed the reaction equilibrium to favorable direction of borate ester of polyoxyalkylenes, formation.

As to the removal method, azeotropic distillation using azeotropic agent and batch or continuous distillation using distillation tower are preferable. Or feuch

For the purpose of improving the pro- proported perties of the borate ester of pelyoxy-polyoxy-lengs alkylenes amino-group containing compounds und and/or solvent may be added to said the borate esters of polyoxyalkylenes.

Adding the amino-group containing com
pound to the borate ester of polyoxy-polyoxyalkyless
alkylenes exhibits the suppliessing of

borate ester hydrolysis and also exhibi
Improves
to rust preventive effect under the con
ditton of exhibits to water or its

vapor.

Examples of the amino-group containing compound include alkylamine, cyclo alkylamine, alkanol amine, heterocyclic amine, diamine, lactam, cyclic imide and poly-polyamine amine, which may be used alone or combination nation selecting from these compound.

As the alkylamine, there can be used methylamine, dimethylamine, trimethylamine, tri—trieflylamine, ethylamine, diethylamine, tri—trieflylethylamine, propylamine, N, N di [poly N, N di [poly (4) oxyethyl] hexadecylamine, dodecyl oxyethylamine, stearamide propyl dimethylamine, stearamide propyl dimethylamine, polyoxyethylene (3-30) oeta ochological decylamine, polyoxyethylene (3-30) lauryl

amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) dilauryl amine, polyoxyethylene (3-30) stearyl amine, polyoxyethylene (3-30) alkyl amine, polyoxyethylene (3-30) dialkyl amine, and di (oleoyloxyethyl) hydroxy amine.

As the cycloalkyl amine, there can be

used cyclohexyl amine, methyl cyclohexyl amine and ethyl cyclohexyl amine.

As the alkanol amine, there can be used ethanol amine, diethyl hydroxy methyl amine, diethanol amine, dimethyl amine— ammochamolethanol, triethanol amine, propanolamine, dimethy 2—hydroxypropyl amine, butanol amine, methyl di (2—hydroxyethyl) amine, tri (2—hydroxyethyl) amine, hydroxymethyl di (2—hydroxyethyl) amine, dibenzil 2—hydroxypropyl di (2—hydroxyethyl) amine, dibenzil 2—hydroxypropyl di (2—hydroxyethyl) amine and cyclohexyl di (2—hydroxyethyl) amine.

As the cycloalkanol amine, there can mellyleycohorand be used cyclohexanol amine, methyleycle—hexanol amine and ethyleyclohexanol amine.

As the heterocyclic amine, there can be used transded pyridine, lutidine, 3,4-xylidine, piperidine, N-methyl piperidine and N-ethyl piperidine.

As the lactam, there can be used propio lactam, N-methylpropio lactam, N-ethyl buthypo lactam, N-methyl varero lactam, N-methyl caprolactam and phenyl caprolactam.

As the cyclic imide, there can be used succinimide, N-methyl succinimide, N-cflylethyl succinimide, phenyl succinimide and 2-undecyl imidazoline.

As the diamine, there can be used ethylene diamine, triethylene diamine and tetraethylene diamine.

As the polyamine, there can be used diethylene triamine, triethylene tetras letras let

Among these aminogroup containing compounds

pound, tertiary aminogroup containing

compounds exhibit accellent effect of

preventing hydrolysis of borate ester of

polyoxyalkylene and promoting the cleamy

ning and purging the coloured contamina

colored contamina

Example of tertiary aminogroup contains in general compounds having above mentioned excellent properties are polyoxyethylene (3-30) octadecyl amine, polyoxyethylene (3-30) (3-30) lauryl amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) oleyl amine, polyoxyethylene (3-30) dilauryl amine, polyoxyethylene (3-30) stearyl amine, polyoxyethylene (3-30) alkyl amine, polyoxyethylene (3-30) alkyl amine, polyoxyethylene (3-30) dialkyl amine.

The amount of aminogroup containing compound to 100 parts by weight of the borate ester of polyoxyalkylene is from 0 to 100 parts by weight, favourably and pefeculy from 5 to 50 parts by weight and most preferbly favourably from 10 to 30 parts by weight.

Use of the solvent contributes to a lower viscosity of the borate ester of polyoxyalkylene.

As the solvent, there can be used water, methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, isopropyl ether, ether, ethylene glycol, polyethylene glycol, polyethylene di-dimethyl

methyl ester, diethylene glycol, tri-frællufad ethylene glycol, ethylene glycol di-time methyl ether, diethylene glycol di- dimelly metbyl ether, diethylene glycol diethyl ether, ethylene glycol dipropyl ether, triethylene glycol dimethyl ether, triethylene glycol monobuthyl ether, diethylene glycol monobutyl ether, di-dictlylene ethylone glycol diethyl ether, diethylo-dullylene pre glycol propyl ether, diethylene col dibuthyl ether, dimethyl ether, pro-propfed pylone glycol, acetone, methyethyl keto- kelmo ne, furfural, dioxane, methane sulfonate, diethy ether, tetra hydrofuran, hexane, acetic anhydride, heptane, octane, nena- wonand ne, decane, undecane, benzene, toluene. xylene, cyclohexane, cyclohexene, dime-dimetry thy formamide, dimethy sulfoxide, hexa hypometh methyl triamide phosphate, acetonitrile, N-methyl pyrrolidone, chloroform and carbon tetrachloride and the solvents used by alone or combination.

The amount of solvent to 100 parts by polycygalkyloul weight of borate ester of polycygalkyloul ene and aminogroup containing compound are respectivery from 0 to 100 parts by weight, favourably from 5 to 50 parts by weight and most favourably from 10 to 30 parts by weight.

The other ingredient other than amine—
group containing compound and/or solvent dowly
may be incorporated to borate ester of
polyoxyalkylene for the purpose of improoving the properties of the release
agent of the present invention.

As the other ingredient, there can be Ingredients

used stabilizer, neutralizer, antiox dant, ultraviolet absorber, light st antistatic agent, lubricant, p-r-o-processabel cessability improving agent filler agent, coupling agent, anti-cop dispersing rusting agent, blowing agent, nu-nuclear ing agent) clear forming agent, pigment, dyeinge agents carbon black, water tree prevent pourty voltage stabilizer, antitras-cuti-tracky king agent, organic peroxide, crosslink-closslink disinfectant, antiseptics, antimold agentq and antirust

In the present invention, a release agent for metallic mold means the release se agent which is coated on the surface of metallic mold used for plastic or gum processing to prevent the adhesion between ween metallic mold and plastic molded function the relate products resulting to make the plastic and molded product to molded product to molded produces to assily separate from the

The metallic molds to which the release agent of the present invention is applicable agent of the present invention is applicable cable, are used for making the parts and structural materials for automobile, au anto bicycles to hicycle, scooter, television, radio, audio equipment, washing machine, rice cooker, personal computer, portable telephone, game machinery, building materials, office supplies, stationery, toys, sports goods, sports equipment, agricultural to fools and marine tools by the method of injection molding, blow molding, compression of the molding, slush molding, fluidized bed coating, flat film extrusion proce-

process processury

The material of mold may be metal or ceramics. Ceramic

Plastics and gum which are processed by using the metallic mold of the present invention are thermoplastics and thermo-setplastics as follows.

As the thermoplastic resin, there be used high density polye, thylene, pressure low density polyte such vinglalcohol as HP-LDPE, EVA, EEA, Ionomer, olefin ylalcohol copolymer, LLDPE, VLDPE, polypropylese (PP) propylene (PP), polystylene (PS), acrylonitrile-butadiene-stylene copoly-copolymer (ABS) mer (ABS), acrylonitrile-stylene copolymer acrylonitrile-butadiene copolymer, (AS), acrylonitrile acrylate-stylene copolymer polyvinyl chloride (PVC), polyamide, methylmethacrylate (PMMA), polyacetal (POM), polyarylate, f luoro. aminopolyacrylamide, polyimide (PI), Opo <u>carbon</u> resin, hismaleimide (PABI), polyamideimide (PAI), polyetherimide (PEI), bismaleimidetriazine resin (BT), polysulfone, polybutylene terephthalate (PBT), polyethylene t thalate (PET), polyvinylidene chloride, polycarbonate (PC), polyvinyl acetate, alcohol, polyvinyl ether, polvvinyl formale, modified polyvinyl polyphenyleneoxide (PPO). polyethersulfone (PESF), (S), polymethylpenten (TPX), liqu polymer, silicone resin, natural rubber (N butyl rubber (IIR), R),

<u>butadiene</u> rubber (NBR), chloroprene rubber (CR), styrene butadiene rubber (SBR), butadiene rubber (BR).

As the thermoset plastic resin, there can be used phenolic resin, urea resin, melamine resin, diallyl phthalate resin, epoxy resin, unsaturated polyester resin, and the like.

The plastic molded products made by using the above mentioned resins are mutaculoused for the parts and structural materials for automobile? autobicycle scoop scotest ter, television radio, audio equipment, washing machine? rice cooker, personal computer? portable telephones game machine machinery nery, building materials, office supplies supplies es, stationery, toys, sports goods, sports equipment, agricultural tools and marine tools.

They are usually prepared by plastic processing methods such as injection molding, blow molding, compression molding, transfer molding, rotating molding, slush molding, inflation tubular film process- processing and extrusion molding.

The release agent of the present invention is prepared using one or more than one kind of borate ester of polyoxyalky-lene.

The release agent may contain amino Compounds and/or solvent. Solvents

The release agent may further contain surface active agent, pigment, die, in inoignocorganic filler, dripping preventable agent, precipitation preventable agent, antioxidant and deformer.

antioxidads def

defermers

The release a glent may be filled in the aerosol container with propellant.

Coating of the release egent of the present invention on the surface of the metallic mode can be conducted by brush problem ing spraying, dipping or contacting the surface with a woven cloth or nonwoven cloth which are has immersed with the release agent.

EXAMPLE

Now, the release agent for metallic molds used mold for forming a plastic molded molded product according to the present invention will be described in further detail with reference to Examples.

However, it should be understood that the present invention is by no means restricted by such specific Examples.

Example 1

Borate ester of polyoxyalkylene expressed by chemical formula (5) was obtained by following synthesis process.

In a 7000 ml flask equipped with three inlet pipe and displaced by nitrogen gas were charged 146g (1 mole) of triethyl borate $[B(OC_2H_5)_3]$, 1.2g of dibutyl tin dilaurate and 500 ml of benzene.

Subsequently, the solution in the flask was added with 664g (2 mole) of tripropyleneglycol triethylenglycol tripropyleneglycol monomethyl ether und 318g (1 mole) of tripropyleneglycol triethylenglycol under stirring condition to obtain uniform blended solution.

Subsequently, the solution in the flask was stirred for 13 hours at 95°C conditions under the condition of distillation, to remove a ethanol and benzene as the by hypotheter product to obtain 989g (0.99 mole) of a borate ester of polyoxyalkylene expressed by chemical formula (5).

In a vessel, 100 parts by weight of a borate ester of polyoxyalkylene expression ed by chemical formula (5), 15 parts by weight of triethyl amine and 10 parts by weight of ethanol were blended for 10 minutes under room temperature to obtain the release agent (1).

The release agent (1) was brushed en the surface of metallic mold for injecting tion molding of polyacetal (POM) resin composition (made by Polyplastic Company Ltd.).

Using above mentioned metallic mold and resin composition, injection mold mold was conducted.

The terms of maintaining the release agat remined

effect of the surface ab

effect of the metallic mold was about 55

hours, the terms which was very long compared

paring to conventional release agent as

shown in the comparative example 1. (1)

The words The terms with maintaining

the release effect of the metallie mold"

means the terms from starting time to

stopping time of injection molding with the

stopping time which is the time of being

observed any one item of phenomenons are observed;

such as accumulating of dirty materials

on the sufface of metallic mold; cloudy

ing of the surface of the metallic mold;

transferry
transferring the shaper or contaminant
from the metallic mold to the plastic
molded product; or transferry contaminates from the websilic
molded product; to transferry contaminates from the websilic
mold to the plastic molded product

Comparative Example 1

According to the same preparation method of Example 1, a release agent (2) consisting 100 parts by weight of high viscosity silicone oil (500 cs at 25°C) and 20 parts by weight of the chlorinated type solvent was prepared. The same releasing test was conducted according to the same condition of example 1.

The terms of maintaining the release agent of the terms of maintaining the release agent of the metallic mold of comparative example 1 was about 10 minutes.

Example 2

Borate ester of polyoxyalkylene expressed by chemical formula (8) was prepared according to the same preparating method (B) except using pentaethylene—
glycol ethylether, instead of tripropyle—tripropylenely neglycol ethylether, instead of tripropyle—tripropylenely ether and tripropyleneglycol monomethyl ether and tripropyleneglycol triethyleneglycol. Then a release agent (3) consisting 100 parts by weight of borate ester of polyoxyalkylenely oxyalkylenes expressed by chemical formula (8) and 20 parts by weight of the pentaethyleneglycol was prepared. The same releasing test was conducted according to the same condition of procedure as

The terms of maintaining the release agent on the metallic mold of example 2 was about 48 hours, the terms which was very long comparing to conventional release agent as shown in the comparative example 1.

Example 3

Borate ester of polyoxyalkylene expressed by chemical formula (14) was prepared according to the ing method Dexcept using p t ripro Lene glycol instead of ol triethylenglycol monomethyl ether tripropyleneglycol triethylen glycol. Then, a release agent (4) consisting 100 poly oxyalkylae parts by weight of borate ester of poly oxyalkylene expressed by chemical formula (14) and 20 parts by weight of the polyoxyethylene (9) dilauryl amine was prepared.. this release agent was lested according to condition of ex-procedure as same effect of the mol hours was about 65 to conventional release agent a s shown in the comparat ve example

ABSTRACT

A release agent for metallic mold for forming a plastic molded product characterized by containing a borate ester of polyoxyalkylene.